

# COATINGS. ENAMELS

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## DEVELOPMENT OF A BASE FOR BOTTOM FRIT FOR ELECTROSTATIC POWDER ENAMELING

L. L. Bragina<sup>1</sup> and O. V. Shalygina<sup>1</sup>

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The optimal ratio of alkali and alkali-earth oxides in  $R_2O - RO - \Sigma(B_2O_3 + SiO_2)$  glasses is determined from the standpoint of achieving the maximum values of the resistivity in them by means of the polyalkali and polycation effects acting in combination:  $2Na_2O : 1K_2O : 1Li_2O$  and  $1BaO : 1CaO$ . It is determined experimentally that  $R_2O - RO - \Sigma(B_2O_3 + SiO_2)$  glasses multialkali silicate glasses with resistivity above  $10^{10} \Omega \cdot m$  can be synthesized by means of the polyalkali and polycation effects. A composition of the bottom frit has been developed for the PUESTA technology with single firing of the bottom and cover layers. This frit is now used in the production of household appliances.

The world enamel industry at its present stage is striving to decrease production costs, increasing making production processes ecologically cleaner, and improving product quality. The PUESTA powder electrostatic enameling technology is the best technology for obtaining competitive high-quality enameled articles while at the same time satisfying stringent ecological requirements and conserving energy and resources [1].

In Ukraine, the powder electrostatics technology has now been adopted at different enterprises, such as "Nord" JSC, "Azovmash" JSC, and "Druzhkovskii zavod gazovoi apparatury" JSC for the production of household gas and electric stoves. All the advantages of the PUESTA technology and its flexibility in the production of various types of enameled articles and equipment parts have made it desirable to extend this enameling method and adopt it at existing enterprises and enterprises which are now being designed.

The problem of synthesizing, on the basis of the raw materials base of Ukraine, glass frit for powder electrostatic enameling is timely and topical. The purpose of the present work was to develop a composition for the glass matrix — the base for the bottom frit for enameling articles made of low-carbon thin-sheet steels — using the PUESTA technology with single firing of the bottom and cover layers.

The following requirements for the properties of enamels were taken into account when choosing the initial glass-

forming system for synthesizing model glasses as the bases for bottom frits for enameling parts made of thin-sheet low-carbon steel by the PUESTA technology followed by single firing of the bottom and cover layers:

high resistivity ( $\rho_v \geq 10^7 \Omega \cdot m$ ) of the enamel glass frits; this is due to the characteristics of the PUESTA technology — the specific nature of the deposition and adhesion of finely dispersed enameled particles in a high-voltage field;

easy-fusibility of the bottom layer — firing temperature of two-layer coatings  $800 - 820^\circ C$ , which substantially decreases energy consumption; the firing temperature of the bottom must be in the range  $790 - 810^\circ C$ .

The present investigations were based on the hypothesis that high resistivity of silicate glasses can be achieved together with easy fusion of the glasses by means of the polyalkali effect, due to simultaneous presence of several alkali cations, and the polycation effect by introducing several alkali-earth cations into the glass compositions.

The system  $R_2O - RO - B_2O_3 - SiO_2$  ( $R_2O$  —  $Na_2O$ ,  $Li_2O$ ,  $K_2O$ ;  $RO$  —  $CaO$  and  $BaO$ ) was chosen as the initial system for synthesizing the glass matrix.

Taking the sum ( $SiO_2 + B_2O_3$ ) as one component of the glass-forming composition, we obtain a pseudoternary system in which the region bounded by the following contents was studied (%<sup>2</sup>):  $55 - 75 \Sigma(SiO_2 + B_2O_3)$ ,  $10 - 30 R_2O$ ,  $0 - 15 RO$  (Fig. 1). Fourteen points were chosen inside this region with an interval of 5% — the model glasses MG1 —

<sup>1</sup> National Technical University "Kharkov Polytechnical Institute," Kharkov, Ukraine.

<sup>2</sup> Here and below — the molar content.

MG14. Table 1 gives the content of the components of the system  $R_2O - RO - \Sigma(B_2O_3 + SiO_2)$  at the points chosen.

The two points MG14 and MG8 were chosen to investigate the influence of the polyalkali and polycation effects on the resistivity of glasses in the indicated region in this system. The point MG14, corresponding to a composition with  $RO = 0$ , was chosen because it is necessary to determine the effect of only alkali oxides in the absence of alkali-earth oxides. The maximum content of glass formers at the point chosen makes it possible subsequently to introduce RO by means of  $SiO_2$ .

To determine the optimal ratio of the alkali components ( $Na_2O : K_2O : Li_2O$ ), five compositions were synthesized at the point MG14, where  $RO = 0\%$ ,  $\Sigma(SiO_2 + B_2O_3) = 75\%$ , and  $R_2O = 25\%$ . To determine the influence of the alkali-earth components CaO and BaO on the change of resistivity and to determine their optimal ratio, five compositions were synthesized at the point MG8, where  $RO = 10\%$ ,  $R_2O = 25\%$ , and  $\Sigma(SiO_2 + B_2O_3) = 65\%$ . The point MG8 was chosen on the basis of the intermediate RO content in it, maintaining the indicated amount of  $R_2O$ . The ratios of the components and the chemical composition of the synthesized glasses are presented in Table 2. This ratio of alkali and alkali-earth components has been chosen because it is necessary to investigate the mutual effect of the alkali cations  $K^+$ ,  $Na^+$ , and  $Li^+$  on the polyalkali effect and mutual effect of the alkali-earth cations  $Ca^{2+}$  and  $Ba^{2+}$  on the polycation effect.

The complex effect of this group of cations on the total change of the electrical resistance of glasses in the system being studied was determined. The following assumptions were also used in these investigations. The electric conductivity of the glasses under the action of an electric field is determined by the fact that the modifying ions which transform the network do not cross arbitrarily from one interval into another, but rather they move in a predominant direction. The univalent ions  $Li^+$  and  $Na^+$ , and to a much lesser extent  $K^+$  ions, make the main contribution to the electric conductivity of glasses at room temperature. The  $Li^+$  and  $Na^+$  ions are relatively small in size and their charge is low, so that they can easily hop in the network and are mobile ions. The substantially lower mobility of  $K^+$  ions is due to their comparatively large ionic radius.

TABLE 1.

Compo- sition	Molar content, %			Molar content, %		
	$\Sigma(SiO_2 + B_2O_3)$	$R_2O$	RO	$\Sigma(SiO_2 + B_2O_3)$	$R_2O$	RO
MG1	55	30	15	MG8	65	25
MG2	60	25	15	MG9	60	30
MG3	65	20	15	MG10	65	30
MG4	70	15	15	MG11	70	25
MG5	75	10	15	MG12	75	20
MG6	75	15	10	MG13	70	30
MG7	70	20	10	MG14	75	25

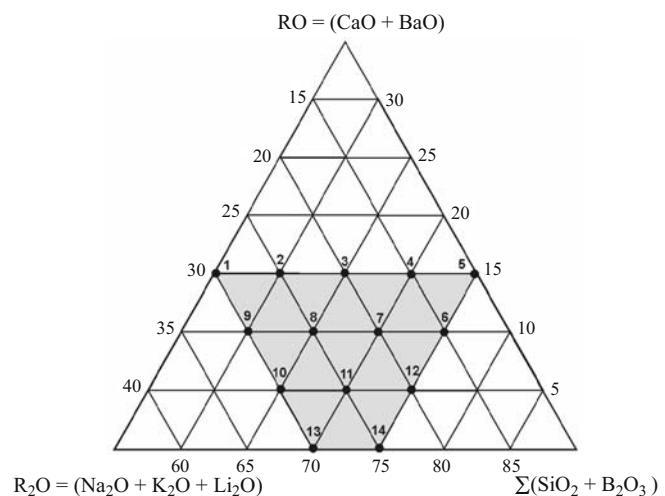


Fig. 1. Region of model glasses in the pseudoternary system  $R_2O - RO - (B_2O_3 + SiO_2)$ : 1 – 14) MG1 – MG14 model glasses, respectively.

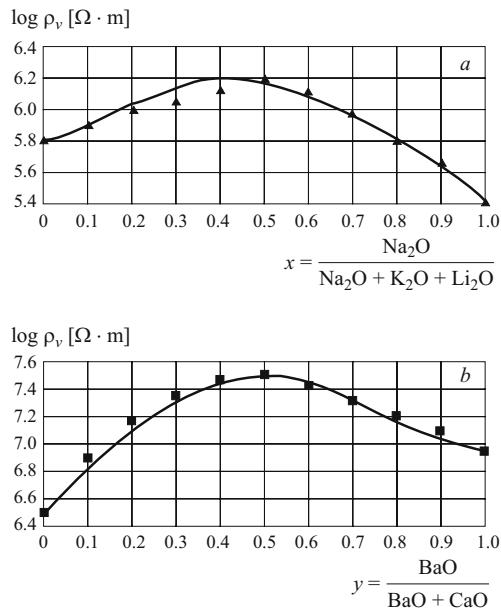
The volume and surface electric conduction is also important for finely dispersed enamel glass powders. The surface electric conductivity of the powders depends on the formation of a thin hydrate film, enriched with the leaching products of the glass, on their surface. As the chemical stability increases, the surface electric conduction decreases and practically vanishes at temperatures above 100°C. The volume electric conductivity of the powders depends on the composition of the glass and temperature.

The volume electric conductivity of enamel is especially important when special bottom frits are used for electrostatic deposition on steel articles. The characteristic quantity here is the reciprocal of the electric conductivity — the resistance. Ordinarily, a high resistance of finely dispersed enamel powders is achieved by depositing hydrophobic organosilicon

TABLE 2.

Composi- tion*	Molar content, %						
	$SiO_2$	$B_2O_3$	$Na_2O$	$K_2O$	$Li_2O$	CaO	BaO
MG14.1	60	15	25.0	0	0	—	—
MG14.2	60	15	0	12.5	12.5	—	—
MG14.3	60	15	12.5	6.25	6.25	—	—
MG14.4	60	15	8.33	8.33	8.33	—	—
MG14.5	60	15	16.66	4.165	4.165	—	—
MG8.1	50	15	12.5	6.25	6.25	0	10.0
MG8.2	50	15	12.5	6.25	6.25	10.0	0
MG8.3	50	15	12.5	6.25	6.25	5.0	5.0
MG8.4	50	15	12.5	6.25	6.25	2.5	7.5
MG8.5	50	15	12.5	6.25	6.25	7.5	2.5

\* For compositions MG14.1 – 14.5:  $\Sigma(B_2O_3 + SiO_2) = 75$ ,  $\Sigma R_2O = 25$ ,  $\Sigma RO = 0$ ; for the compositions MG8.1 – MG8.5:  $\Sigma(B_2O_3 + SiO_2) = 65$ ,  $\Sigma R_2O = 25$ ,  $\Sigma RO = 10$ .



**Fig. 2.**  $\log \rho_v$  at  $200^\circ\text{C}$  versus the ratios of the alkali oxides  $\text{Na}_2\text{O} : \text{K}_2\text{O} : \text{Li}_2\text{O}$  in the series of glasses MG14 (a) and alkali-earth oxides  $\text{BaO} : \text{CaO}$  in the series of glasses MG8 (b).

films, which are characterized by resistivity  $\rho_v \geq 10^{13} - 10^{15} \Omega \cdot \text{m}$ . As a result of the low hardness and durability of and therefore substantial damage to organosilicon films during shipment and deposition and to increase adhesion of the powders, glass frit with high electric resistance was obtained in the present work.

As noted in [2, 3], in potassium – sodium – silicate glasses an increase of the resistance is most strongly expressed when three alkali oxides are present simultaneously in the ratio  $2\text{K}_2\text{O} : 1\text{Li}_2\text{O} : 1\text{Na}_2\text{O}$ , which is used to obtain electrically insulating glasses and coatings. However, in the mass production of bottom enamels for low-carbon steels, the alkali flux components for a host of reasons are introduced predominantly via  $\text{Na}_2\text{O}$ ;  $\text{K}_2\text{O}$  and  $\text{Li}_2\text{O}$  are used to a much lesser extent. Consequently, we investigated the possibility of achieving maximum resistance of  $\text{R}_2\text{O} - \text{RO} - \Sigma(\text{B}_2\text{O}_3 + \text{SiO}_2)$  glasses with the  $\text{Na}_2\text{O}$  predominating.

The following compositions were synthesized at the point MG14 to determine the influence of the ratio of the alkali cations on the polyalkali effect:

MG14.1, where the entire amount of alkali oxides is introduced only via  $\text{Na}_2\text{O}$ ;

MG14.2 with zero  $\text{Na}_2\text{O}$  content and equimolar  $\text{K}_2\text{O}$  and  $\text{Li}_2\text{O}$  content;

MG14.3, where, by analogy to the polyalkali effect studied in [2], for three alkali components  $2\text{K}_2\text{O} : \text{Li}_2\text{O} : \text{Na}_2\text{O}$ , glass with the ratios  $2\text{Na}_2\text{O} : 1\text{K}_2\text{O} : 1\text{Li}_2\text{O}$  was synthesized;

MG14.4 with  $\text{Na}_2\text{O} : \text{K}_2\text{O} : \text{Li}_2\text{O} = 1 : 1 : 1$  (this glass was made taking account of R. Mueller's assertion [4] that silicate glasses with equimolar ratios of the three alkali components have the highest resistance);

MG14.5 with  $\text{Na}_2\text{O} : \text{K}_2\text{O} : \text{Li}_2\text{O} = 2 : 0.5 : 0.5$ .

The volume resistivity  $\rho_v$  of the glass powders studied was measured in the temperature regime  $20 - 300 - 20^\circ\text{C}$ . This measurement regime is used not only because it is necessary to eliminate the effect of surface moisture in order to establish the true values of the resistance of the glasses but also to study the character of this phenomenon. Ensuring that moisture has no effect on the resistance of the experimental glasses, the results of the determinations at  $200^\circ\text{C}$  were taken into account in the analysis of the effect of the glass composition on the polyalkali and polycation effects.

### Volume Resistivity of the Powders of the Model Glasses

Model glass	$\log \rho_v$ at $200^\circ\text{C}$
MG14.1	5.40
MG14.2	5.80
MG14.3	6.19
MG14.4	6.05
MG14.5	5.95
MG8.1	6.51
MG8.2	7.00
MG8.3	7.50
MG8.4	7.28
MG8.5	7.17

Figure 2a displays  $\log \rho_v$  at  $200^\circ\text{C}$  versus the alkali oxide ratio in the model glasses. The curve obtained  $\log \rho_v = f(x)$ , where  $x = \frac{\text{Na}_2\text{O}}{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O}} = 0, \dots, 1$ ,

shows that the polyalkali effect in this system is strongest in glasses where  $2\text{Na}_2\text{O} : \text{K}_2\text{O} : \text{Li}_2\text{O}$  (MG14.3).

Thus, it has been determined that easily fused enamel frits with high volume resistivity which contain equimolar quantities of  $\text{Na}_2\text{O}$  and  $\Sigma(\text{K}_2\text{O} + \text{Li}_2\text{O})$  can be easily obtained. For this reason, the glass MG14.3 with the established alkali-oxide ratio  $2\text{Na}_2\text{O} : \text{K}_2\text{O} : \text{Li}_2\text{O}$  into which  $\text{BaO}$  and  $\text{CaO}$  were introduced was chosen for further study. It is shown in [2, 4, 5] that the introduction of large modifying cations  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , and others, which J. Stevels called immobile, into alkali-containing glasses decreases the conductivity of these glasses. The compounds  $\text{CaO}$  and  $\text{BaO}$  are of greatest interest and practical value for synthesizing commercial glass enamels. Taking account of these data, five glass compositions with a constant content of the glass-forming components as well as sums of alkali and alkali-earth oxides were synthesized within the limits of the system studied (see Table 2). Since the ratio of  $\text{Ba}^{2+}$  is larger, the polycation effect was studied with different  $[\text{BaO}]$  to  $\Sigma[\text{BaO}] + [\text{CaO}]$  ratio.

Figure 2b displays the curve  $\log \rho_v = f(y)$  for MG8 series glasses, where  $y = \frac{\text{BaO}}{\text{BaO} + \text{CaO}} = 0, \dots, 1$ . The maximum on this curve, attesting to the strongest polycation effect, corresponds to the MG8.3 composition with equimolar ratio of

the alkali-earth oxides BaO and CaO. Comparing the positions of the maxima on the curves (see Fig. 2) clearly shows that the alkali-earth cations make a substantial contribution to the increase of the resistance of alkali – alkali-earth – silicate glass. It is important to underscore that the introduction of BaO and CaO into alkali-silicate glasses where the alkali ratio is set by SiO<sub>2</sub> — the component that ordinarily increases the resistivity  $\rho_v$  — led to a substantial increase of the value of  $\log \rho_v$ .

The explanation of the effect of the chemical composition of the glasses studied, specifically, their content of alkali and alkali-earth cations and their ratios, on the resistivity of R<sub>2</sub>O – RO –  $\Sigma(B_2O_3 + SiO_2)$  glasses is based on fundamental assumptions about the nature of conduction in glasses.

According to B. Lengyel [6], when an electric field is imposed, electricity is transferred by means of “hopping” to surrounding free or freed sites as a result of the displacement of mobile ions (in alkali-borosilicate glasses — alkali cations). To move from their sites they must possess the required activation energy  $E_\alpha$  for electric conduction. This energy characterizes a potential barrier which cations moving in the direction of the electric field must overcome. According to J. Stevens [5], the activation energy for current hops depends on the structural strength of the Si – O network of the silicate glass  $Y = [O]/[Si]$  and on the nature of the mobile cations. As  $Y$  decreases, the network becomes weaker and  $E_\alpha$  should decrease. According to B. Lengyel [6], the activation energy for electric conduction of “mixed” glasses, containing several alkali cations simultaneously, is always higher than the value for “pure” glasses with one type of charge-carrier cation, since ions participating in the transfer of electricity at a braking effect on one another. For “pure” glasses the free sites present in the structure are equivalent, while for “mixed” glasses (because the sizes of the charge-carrier ions are different) the larger cations must occupy sites previously occupied by a smaller ion, which is geometrically problematic. Therefore, mixed transitions increase the activation energy.

In summary, when three cations with different sizes are introduced simultaneously into silicate glass a structure with the highest possible density is formed and, therefore, the activation energy will reach its maximum value in this case. The cations Ca<sup>2+</sup> and Ba<sup>2+</sup> which are introduced appreciably decrease the mobility of the univalent cations, which results in an even larger increase of the activation energy. It should be underscored that these laws were established for monolithic glasses. In our work, we investigated glass powders, since the technology for electrostatic deposition of coatings presupposes the use of finely dispersed enamel powders with particle size 3 – 60  $\mu m$ . Since glass powders have a high resistivity and relatively low chemical stability, they are often coated with hydrophobic polymer films to decrease the influence of moisture and to increase the resistivity. As a result of the substantially lower hardness and abrasion resistance of polymer films as compared with enamel glasses, these films

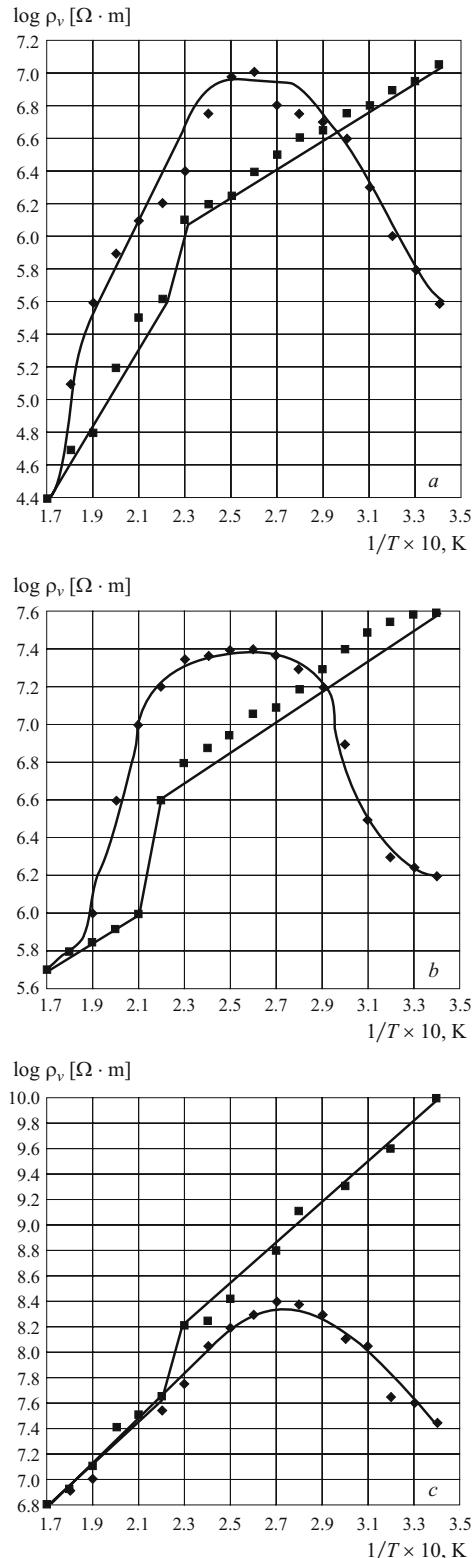


Fig. 3. Temperature dependence of the electric resistance of MG14.1 (a), MG14.3 (b), and MG8.3 (c) glasses.

become worn and lose their continuity during shipment and repeated use. As a result of contact between the moisture in the surrounding medium and the bared sections of the glass

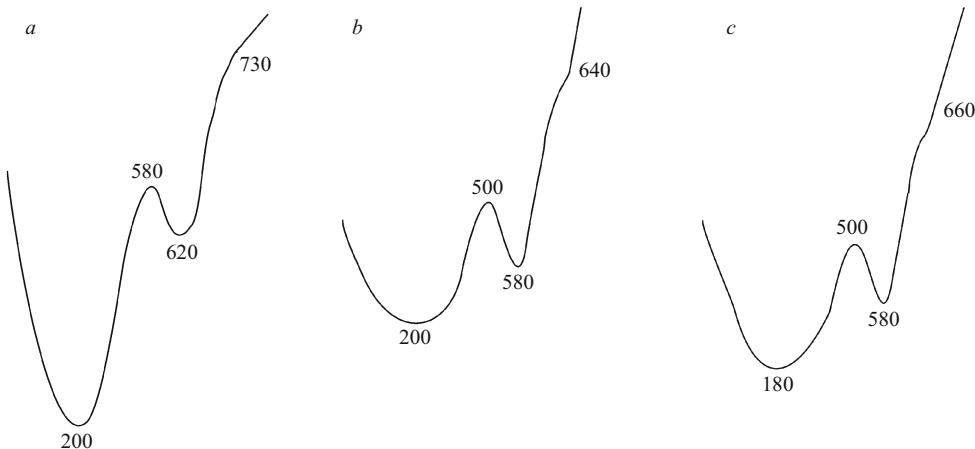


Fig. 4. Thermograms ( $^{\circ}\text{C}$ ) of the MG14.1 (a), MG14.3 (b), and MG8.3 (c) model glasses.

particles, a hydrate film forms on the surface of such sections and subsequent leaching of the glass can occur.

To check these suppositions experimentally for the model glass systems studied  $\text{R}_2\text{O} - \text{RO} - \Sigma(\text{B}_2\text{O}_3 + \text{SiO}_2)$  it was necessary to obtain data on the activation energy of electric conduction in such glasses. To this end, the temperature dependence of the volume resistivity of MG14 and MG8 series glasses was studied (see Table 2). Figure 3 displays the functions  $\log \rho_v = f(1/T)$  obtained in the temperature regime  $20 - 300 - 20^{\circ}\text{C}$  for powders with the following characteristic model-glass compositions:

MG14.1 — as containing only one type of current-carrying alkali cations;

MG14.3 — as a composition with three types of alkali cations in the ratio ensuring the strongest polyalkali effect;

MG8.3 — containing alkali-earth cations in addition to alkali cations.

It was established that two different types of curves  $\log \rho_v = f(1/T)$  obtained on heating and cooling are common to the experimental glasses.

On heating, the function  $\log \rho_v = f(1/T)$  exhibits the same curvilinear character: the electric resistance of glass powders increased with temperature increasing from  $20^{\circ}\text{C}$  on average to  $100^{\circ}\text{C}$ , and then on heating to  $300^{\circ}\text{C}$  the values of  $\rho_v$  decreased. The low values of  $\rho_v$  of finely dispersed glass powders at  $20^{\circ}\text{C}$  and the increase of the values of the resistance on average to temperature  $90^{\circ}\text{C}$ , evidently, are due to the large effect of surface conduction on this property. The behavior of the curves  $\log \rho_v = f(1/T)$  on cooling was characterized for all compositions by the presence of S-shaped inflections. For the characteristic glasses this inflection is recorded in the temperature range  $200 - 160^{\circ}\text{C}$ . The existence of such inflections is atypical for the temperature curves of the resistance of monolithic glasses [1, 2]. Their presence can be explained by using model glasses in the form of finely dispersed powders. In this case, the effect of moisture is greater than for monolithic glasses.

Analysis of the experimental data shows that there is a relation between the sharp jump of the resistivity  $\rho_v$  when the samples are cooled and the increase of conduction at this temperature when the samples are heated. It was determined that the surface conduction on heating ( $\rho_v$  increases) for MG14.1, MG14.3, and MG8.3 glasses decreases on average to temperature  $80 - 100^{\circ}\text{C}$ . The decrease of the moisture content of glass powders is confirmed by the presence of low-temperature endo effects on the DTA curves of the corresponding powders (Fig. 4).

It was determined that the moisture resistance of finely dispersed powders of the experimental glasses, which is characterized by an increase of the resistance  $\rho_v$ , increases when the polyalkali effect (MG14.3) and then the polycation effect (MG8.3) appear, which is due to displacement of the endo effects, due to the removal of moisture from the corresponding glasses, to the region of low temperatures (see Fig. 4). Next, a horizontal section extending to temperatures  $130 - 150^{\circ}\text{C}$  appears on the heating curves  $\rho_v = f(1/T)$ . On subsequent heating to  $300^{\circ}\text{C}$ ,  $\rho_v$  drops sharply as a result of volume conduction in accordance with the equation [4]

$$\alpha = Ae^{-E_a/RT},$$

where  $A$  is a constant pre-exponential factor,  $e$  is the base of the natural logarithm,  $E_a$  is the activation energy,  $\text{kJ}/\text{mole}$ ,  $R = 8.31 \text{ kJ}/(\text{mole} \cdot \text{K})$  is the universal gas constant, and  $T$  is the temperature, K.

Eliminating the effect of surface conduction  $\alpha$ , we calculated for the experimental glasses on each rectilinear section, obtained on cooling, of the curves using the equation [7]

$$\log \frac{\rho_{v2}}{\rho_{v1}} = \frac{E_a}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

where  $\rho_{v1}$  and  $\rho_{v2}$  are, respectively, the values of the volume resistivity of the model glasses corresponding to the temper-

**TABLE 3.**

Glass	$E_a$ , kJ/(mole · K)	$\log \rho_v$	Presence of effect
MG14.1	20.9	5.4	—
MG14.3	25.6	6.2	Polyalkali
MG8.3	36.2	7.5	Polyalkali + polycation

atures  $T_1$  and  $T_2$ ; 2.303 is the ln-to-log conversion factor;  $R = 8.31 \text{ kJ}/(\text{mole} \cdot \text{K})$ .

The activation energy of electric conduction was calculated for MG14.1, MG14.3, and MG8.3 glasses. The characteristic kinks, noted above (see Fig. 3), in the curves  $\log \rho_v = f(1/T)$  were taken into account.

The results of these calculations showed that the increase of  $\rho_v$  in the experimental glasses when the second and third alkali oxides are introduced is correlated with the increase in  $E_a$ . The values of the activation energy of electric conduction and  $\log \rho_v$  at 200°C in the model glasses are presented in Table 3.

This tendency remains when alkali-earth oxides are subsequently introduced into the model glasses. The experimental data agree with the interpretation of the polyalkali and polycation effects as being due to hindered transitions of charge carriers — alkali-metal cations — as the glass structure is compacted as a result of ions with different sizes being embedded in it [7].

In summary, the optimal ratio of alkali and alkali-earth oxides in  $\text{R}_2\text{O} - \text{RO} - \Sigma(\text{B}_2\text{O}_3 + \text{SiO}_2)$  glasses has been de-

termined from the standpoint of maximizing their volume resistivity by enabling the polyalkali and polycation effects to occur together:  $2\text{Na}_2\text{O} : 1\text{Ka}_2\text{O} : 1\text{Li}_2\text{O}$  and  $1\text{BaO} : 1\text{CaO}$ . It has been shown experimentally that multialkali silicate glasses in the system  $\text{R}_2\text{O} - \text{RO} - (\text{B}_2\text{O}_3 + \text{SiO}_2)$  with resistivity  $\rho_v > 10^{10} \Omega \cdot \text{m}$  can be synthesized by means of the polyalkali and polycation effects. A composition for the bottom frit was developed for PUESTA technology with single firing of the bottom and cover layers, and it has been adopted in the production of household appliances [8].

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